Letters to the Editor

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Computation of dipolemoment in the state of polar-nonpolar liquid mixture

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All existing procedures for computing the electric dipolemoment of a polar solute in a nonpolar solvent involve either numerical complications or personal judgements regarding extrapolation and curve fitting etc. (LeFe'vre 1950, Guggenheim 1951). A straightforward and simpler treatment is recommended The value of μ thus calculated are found to be in good agreement with the reported ones.

In the process of derivation we obtain a physical parameter Y_{12}, solely expressed interms of experimentally determined quantities ϵ_{12}, the dielectric constant, n_{12}, the refractive index which nicely represents every stage of dilution as depicted by well defined plots of Y_{12} against w_2 (figure 1).

Retaining all the suppositions there in the Guggenheim's transformed equation of Debye (Guggenheim 1949) for quasi-isolated state of polar-nonpolar liquid mixture in terms of weight fraction w_2 can be written as

$$\frac{\epsilon_{12}-n_{12}^2}{(\epsilon_{12}+2)(n_{12}^2+2)} = \frac{\epsilon_1-n_1^2}{(\epsilon_1+2)(n_1^2+2)} + \frac{4\pi N\mu^2}{27kTM_2} d_{12}w_2. \quad \ldots (1)$$

where suffix 1, 2 and 12 represent solvent, solute and solution respectively and the other symbols have their usual meanings.

Now, on the basis of approximate proposition of Guggenheim, the supposition, that the partial molar volume of the dipole compound and that of the solvent are independent of the concentration (Guggenheim 1949, Böttcher 1952) the density d_{12} is to be expressed as an explicit function of w_2 and thus

$$d_{12} = \frac{W_1+W_2}{V_1+V_2}$$

$$= \frac{d_1}{1-bw_2} \quad \ldots (2)$$

since $w_1+w_2 = 1$, where W_1, W_2; V_1, V_2 and w_1, w_2 are the weights, volumes and weight-fractions of solvent and solute respectively and $b = 1-(d_1/d_2)$, a constant as the densities d_1 and d_2 of solvent and solute are constants.

Using eq. (2) and representing

$$\frac{\epsilon_{12}-n^2_{12}}{(\epsilon_{12}+2)(n^2_{12}+2)} = Y_{12} \quad \text{and} \quad \frac{\epsilon_1-n_1^2}{(\epsilon_1+2)(n_1^2+2)} = Y_1$$

we now have a convenient form of equation (1) as

$$Y_{12} = Y_1 + \frac{4\pi N\mu^2}{27kT} \cdot \frac{d_1}{M_2} w_2(1-bw_2)^{-1} \quad \ldots (3)$$

or, $$Y_{12} = Y_1 + \frac{4\pi N\mu^2}{27kT} \cdot \frac{d_1}{M_2} w_2(1+bw_2+b^2w_2^2+b^2w_2^3+\ldots) \quad \ldots (4)$$

The series of eq. (4) is convergent in the range $0 \leqslant w_2 < 1$ and $\frac{4\pi N\mu^2}{27kT} \cdot d_0$ by R, the above equation reduces to

$$Y_{12} = Y_1 + Rw_2 + Rbw_2^2 + Rb^2w_2^3 + \ldots \quad \ldots (5)$$

The above equation is a well known expression of polynomial function of w_2 of the form

$$Y_{12} = a_0 + a_1w_2 + a_2w_2^2 + a_3w_2^2 + \ldots \quad \ldots (6)$$

If the experimental facts be presented in the form of a plot expressed by eq. (6) one should obtain the dipolement μ simply by comparing the coefficients of equal powers of w_2 i.e.

$$R = a_1 \quad \ldots (7)$$

$$Rb = a_2 \quad \ldots (8)$$

etc.

The constant a_0 represents the intercept and also the experimental physical state of the solution when $w_2 = 0$ as we calculate it from regression analysis (i.e. $a_0 \sim Y_1$). It is, however, pointed out that none would come to the same conclusion by comparing Rb with a_2 etc., since in this case, the second coefficient Rb contains the terms due to orientation effect and relative density effect of solvent and solute Whereas in the experimental plot, apart from the about factors, a_2 is influenced by dipole-dipole interaction, association etc. Thus we are left only with eq. (7) in order to compute the dipolemoment of polar solute,

$$\mu = \sqrt{\frac{27kT}{4\pi N} \cdot \frac{M_2}{d_1} a_1} \quad \ldots (9)$$

From eq. (5) it is obvious that the influence ofhigher order terms is negligible, the curve between Y_{12} and w_2 (figure 1) can practically be expressed in a finite number of terms and the resulting plot is, in general, a parabola.

We have calculated the value of Y_{12} for the systems indicated in column 1 of Table I against different w_2 values and the plots are shown in figure 1.

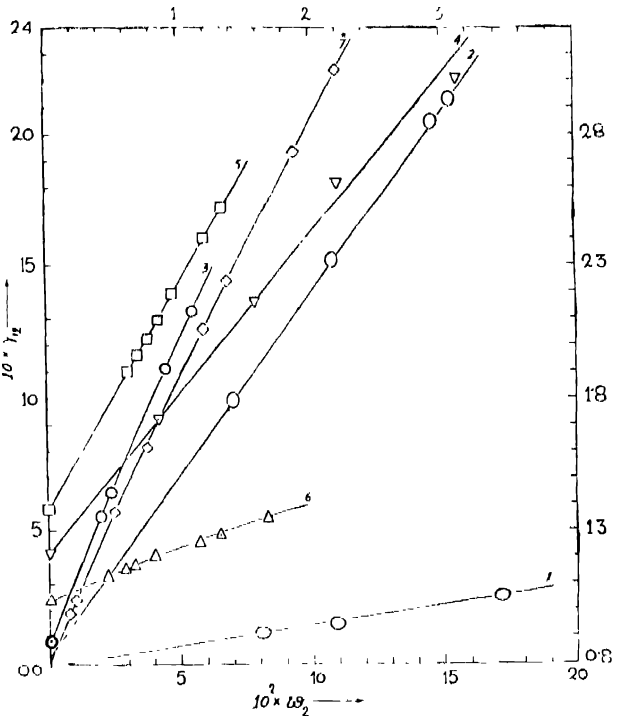

Fig. 1. Plot of Y_{12} against w_2 (weight fraction)
$Y_{12} = 11 \times 10^3$ for the curve N_0. 7A is indicated by the origin of the left side vertical scale. Scale for curves Nos. 1 and 2 is shown on the top and right hand side of the figure. Remaining plots have been represented in the conventional way.

For systems Nos. 1, 2, 4 and 5 the plots are incidentally straight lines but for the remaining systems Nos. 3, 6 and 7 the plots are distinctly pararbola. As all these forms of curves can clearly be expressed by the functional form of the p-th. order polynomial in general the formercurves are the parabola of first degree while the latter ones of second degree.

Linear equations of the Least Square fitting have been solved by using well known Cramer's rule. Finally with the determined values of a_0 and other known parameters of eq. (9), the μ of seven polar solutes have been calculated and placed in Table I for comparison with the reported data published elsewhere.

After a large number of survey on different systems, we conclude that as an observational fact the plot $Y = f(w_2)$ is a monotonically increasing function of w_2 and each one is fortunately a special case of parabola of degree p.

Table 1

Nos.	System	Molecular weight M_2	t°c	d_1(g.cm^{-3})	a_1	$\mu(D)$ Computed	$\mu(D)$ Reported
1.	1:4 Dichloronaphthalene in Benzene	199.09	25	0.8738	0.007095	0.48	0.48[a]
2.	2:7 Dichloronaphthalene in Benzene	199.09	25	0.8738	0.069316	1.52	1.56[a]
3.	1:8 Dichloronaphthalene in Benzene	199.09	25	0.8738	0.24268	2.84	2.82[a]
4.	Diethyl ether in Cyclohexane	74.12	20	0.7784	0.11744	1.27	1.29[b]
5.	Phenol in Benzene	94.11	22	0.87646	0.16670	1161	1.59[a*] 1.62[c]
6.	Tri ethylamine in Benzene	101.00	25	0.874	0.0454	0.87	0.87[a]
7.	Aniline in 1:4 Dioxan	88.36	25	1.028	0.21991	1.67	1.75[d]

Note—Super-subscript *a* stands for the value of μ calculated by Guggenheim (1949, 1951), *a** for the value of μ calculated on the basis of Guggenheim's method (1949) as reported by Böttcher (1952), *b* for the value of μ as reported in page 531 by Glasston (1962), *c* for the value of μ calculated on the basis of Cohen Henriquez formula as reported by Böttcher (1952), and *d* for the value of μ calculated by Few and Smith (1949) assuming distortion polarisation to be 1.05 molecular refraction [R_D].

In the usual procedure of extrapolation it was the general tendency to take the ratio of the difference of dependent variables

$$\left(\frac{\epsilon_{12}-}{2} \quad \text{or} \quad {n_{12}}^2-{n_1}^2 \quad \text{etc.}\right)$$

with respect to the independent variables x_2 (mole fraction) or w_2 etc.; that is the usual style was to take the advantage of the calculus of finite difference.

In our approach no ratio of the dependent-independent variables is included as they are not merely the ratio of two numbers. A single Least Square fitting on Y_{12} against w_2 seems a better simplification over usual treatments where at least two least square fittings (LeFe'vre 1950) Guggenheim 1951) were necessary in order to compute μ of polar solute. This obviously make the manipulation time saving and convenient, because the inaccuracy introduced due to a single least square fitting is less.

It would not be out of context to mention here that the value of μ for Triethylamine in benzene determined by LeFe'vre was 0.91D and that by Guggenheim was 0.87D was due to the different techniques employed in smoothing and consequent extrapolation based on individual judgement (Guggenheim 1951). The

striking feature of the proposed method is manifested in resolving the above controversy. In addition to this, a_1 is only an experimental parameter of the curve and so the specific information regarding the determination of μ is independent of the range of concentration chosen. The probable error introduced in a_1 due to least square is calculated, for example, in case of 1 : 4 dichloronaphthalene in benzene is 0.00027 (3°/$_o$) and that of Phenol in Benzene is 0.2°/$_o$ only, whereas the inaccuracy incurred about 9°/$_o$ in the second term of eq. (9) of Smith's statement (Smith 1950), which is very much similar to the expression a_1 of our case. The greater accuracy achieved in our case is due to the partial or complete compensation of errors as the function is expressed in the form of division of the measured physical parameters. The only further experimental quantity on which μ depends is d_1 as the remaining terms are constants. In the measurement of d_1 an accuracy somewhat better than a_1 is expected. The values of μ thus computed are in excellent agreement with the reported ones suggest this method is not over simplified.

Lastly we deem it proper to mention the remark made by LeFe'vre that the applicability of this method is limited to cases except when the value of B is larger or μ is small, where $B = \frac{v_{12} - v_o}{w_2}$; v = specific volume and w_2 = weight fraction. Thus the discripency noted in the values of μ calculated by us and that reported in the literature for Aniline in 1·4 Dioxan may be attributed to the volume change on mixing.

Our statement of separating effect of dipole orientation term from th eother interaction in the form of a sum of a series (eqs. (5) and (6)) helps the experimenters to visualise the problem in a way that it is possible to estimate dipole-dipole interaction from the coefficient a_2 of the experimental curve as deviation from ideal one where the dipoles are treated to be free from one another.

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